PETROLEUM ENVIRONMENTAL RESEARCH FORUM PROJECT 92-19

"The Origin and Fate of Toxic Combustion Byproducts in Refinery Heaters: Research to Enable Efficient Compliance with the Clean Air Act."

FINAL REPORT August 5, 1997

All 20 participating entities of the Petroleum Environmental Research Forum's Project No. 92-19 Cooperative Research and Development Agreement offer their heartfelt thanks to the members of the Final Report Subgroup for their leadership in the preparation of this summary document reflecting the landmark, seminal new knowledge that arose out of that archetypal Government-University-Industry collaboration. The members of the Final Report Subgroup were Robert Gemmer, Gas Research Institute, Chairman; John Cain, Chevron; Robert Kubo, Southern California Gas Company; and Winnie Torres-Ordonez, Amoco. Additionally, all the participants wish particularly to thank the Southern California Gas Company for providing the support that enabled the exemplary efforts of Ryan Oba, Technical Writer, to whom both the PERF 92-19 CRADA participants and the Final Report Subgroup members offer their heartfelt thanks for doing all the work!

NOTE

Although it contains Protected CRADA Information, as Founding Chairman of the PERF 92-19 CRADA Technical Advisory Committee and in accordance with the prerogative granted me by the PERF 92-19 Executive Committee, this report is released on behalf of the CRADA-Signatory Company Representatives; viz., Robert Andrew, Mobil; Kenneth Comey, Texaco; Robert Gemmer, Gas Research Institute; Robert Kubo, Southern California Gas Company; Harry Tang, Shell; and Winnie Torres-Ordonez, Amoco.

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INTRODUCTION

In 1990, the United States Congress amended the Clean Air Act (CAA). Section 112 of the CAA requires the Environmental Protection Agency (EPA) to develop maximum achievable control technology (MACT) emission standards for Hazardous Air Pollutants, or "air toxics," for certain stationary sources by November 2000.

The CAA identified 188¹ compounds as air toxics. Since combustion is a potential source for many of these compounds, the MACT emission standards will affect the use of process heaters and boilers.

Although these standards are a reasonable way to regulate emissions, good regulations also require a solid scientific foundation. Unfortunately, this foundation did not exist at the time of the CAA amendment.

Prior to 1992, most studies of process heaters and boilers were designed to assess the risk due to toxic emissions at a specific site. Thus, they focused on the operations of particular units and often omitted many of the parameters needed to extrapolate from their data. They also employed methods and calculations that differed from those needed to understand the combustion process. These limitations rendered pre-1992 studies inappropriate to serve as a basis for the nationwide regulation of process heaters and boilers.

The need for a new study was recognized by the petroleum industry, university researchers, and the EPA. This study would differ from previous studies both in scope and objective. It would be the first study whose data and results could be applied to national regulation. It would examine the combustion process in detail, using both laboratory-scale experiments and full-scale burner simulations. It would also review the field data that did exist, to affirm that its results were, in fact, applicable to real world process heaters and boilers.

This study was initiated in 1992 as the Petroleum Environmental Research Forum (PERF) Project 92-19. Project 92-19 was a cooperative research and development agreement (CRADA) between the Department of Energy (DOE) Office of Industrial Technologies and industrial partners Amoco, Chevron, the Gas Research Institute (GRI), Mobil, Shell, the Southern California Gas Company, and Texaco. It was hoped that this study would finally provide the scientific base necessary for sensible, appropriate regulation.

Most of the work took place at Sandia National Laboratories/Livermore (SNL), and Lawrence Livermore National Laboratory (LLNL). The University of California, Los Angeles (UCLA) Chemical Engineering Department collaborated with this study under a separate agreement. Participants contributed their resources and expertise over a four year period to examine different aspects of the combustion process.

OVERVIEW

The purpose of PERF 92-19 was:

¹ Originally there were 189 HAPs. Caprolactum was delisted in 1996.

To generate the best possible data using the best possible science for the best possible regulations.

This data would be used to develop MACT requirements for industrial process heaters and boilers.

The specific objectives within PERF 92-19 were:

- 1. To measure emissions while operating different full-scale burners, including a Conventional Diffusion Flame Burner (CDFB), and a Low-NOx Diffusion Flame Burner (LDFB), under various operating conditions.
- 2. To analyze the emissions data from the preceding objective to predict and identify low air toxic operating conditions.
- 3. To develop new chemical mechanisms and predictive models for the formation of air toxic species that better explain the origin and fate of these species in industrial process heaters and boilers.
- 4. To review the existing field data to assess the applicability of the experimental measurements and new models to real world combustors.

To meet these objectives, the program was divided into three tracks:

The burner experimental track gathered baseline information for different industrial burner designs. It also documented the effects of different process gas fuel mixes and operating conditions on these burners. This track was conducted at Sandia's Burner Engineering Research Laboratory (BERL).

The chemical mechanism track, conducted at LLNL, established new chemical mechanisms by which air toxic species are produced and destroyed. Additional data for mechanism development were gathered using laboratory scale flames at SNL and UCLA.

The field data analysis track reviewed the data from previous field studies to relate the combined information from the previous two tracks with industrial real-world experience. Cases where the field data did not agree with the study results were further examined to establish the cause of the disagreement. This track was performed at SNL.

PERF 92-19 FINDINGS

- The burner experiments showed that under most operating conditions, a properly maintained burner produces exceedingly low levels of hazardous air pollutants, far lower than existing field data would seem to indicate.
- Both Conventional Diffusion Flame Burners (CDFBs) and Low-NOx Diffusion Flame Burners (LDFBs) produce low levels of air toxics. Although time limitations prevented other burner designs from being tested, all experimental and theoretical evidence indicates that most other burner designs will behave in a similar manner.
- No significant difference in air toxic emissions was revealed between burning natural and process gas.

- The new chemical kinetics mechanisms developed and tested at LLNL, SNL, and UCLA support the burner experimental track results.
- Although some discrepancies cannot be discounted, the experimental results generally concur with available field data.

The study data demonstrate that a properly maintained burner is a low toxics burner by design. Tests at the BERL showed that this holds true even when the burner is subjected to severe mixing failures. The studies at BERL also compared modern, Low-NOx Diffusion Flame Burners (LDFBs) with Conventional Diffusion Flame Burners (CDFBs). The differences between the two were insignificant, with both burners producing comparable levels of air toxics.

New chemical kinetics mechanisms developed and tested at LLNL, SNL, and UCLA affirm the BERL results. Although toxic species are initially produced in significant amounts within a jet flame, these species are quickly consumed, even before continued mixing provides stoichiometric air.

Overall, the three tracks show that minimal air toxics emissions are normal and expected from gas-fired combustion systems. Whether the fuel is process gas or natural gas makes little difference; if organics are adequately mixed with oxygen at an adequate temperature, organics are destroyed--even when conditions within the combustion chamber release high levels of unburned hydrocarbons into the post-flame section.

QUALITY ASSURANCE AND CONTROL (QA/QC)

PERF Project 92-19 was initiated to provide good science for good regulations. Since good science in turn depends upon both proper documentation and high quality data, a well-constructed, comprehensive quality assurance plan was vital to the project's success.

Another reason for a solid QA plan was a need to distinguish our study from previous efforts. After the CAA amendments, many opinions regarding the new regulations were formed by extrapolating from the existing data. If the results of our study challenged those opinions, we would be obligated to show that this project was conducted with an unprecedented level of quality assurance and scientific rigor.

Two of our three project tracks generated new data (the *field data analysis track* reviewed existing work). Working with the EPA, we developed a Quality Assurance Project Plan (QAPP) to ensure that:

- All planned measurements had the levels of precision, accuracy, and completeness required to meet the project objectives.
- Quality control procedures were sufficient to ensure the preceding objective.
- The data generated would be defensible if challenged on technical grounds.

We decided that the final work done for the *burner experimental track* should be performed at EPA Category II, appropriate for results used to complement, or in combination with, other projects of similar scope for rule making or policy making. The air toxics targeted by this track included volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and

aldehydes. The QA objectives, as well as analytical methods for these species are listed in Table 1.

The *chemical mechanism track* consisted primarily of scientific and technical development. As in Category II QA, all work was extensively documented and each measurement supplemented with full QA/QC. However, since this track had a research, rather than a regulatory focus, the QA requirements were more broadly defined. Because of this, the QA/QC level of this track, as well as preliminary work in the burner experimental track, were performed according to EPA Category III guidelines.

Table 1 - QA Objectives for Air Toxics Emissions Measurements

Measurements	Sampling/ Analytical Method	Analytical Precision (%)	Data*	Overall Precision (%)	Data*	Accuracy (%)	Data*	Complete- ness (%)
Heavy VOCs (1)	EPA SW846 Draft M0031/ EPA SW846 M8240	± 30	DA MS	± 30	ТМ	± 35	MS/ PAS	100**
Light VOCs (1)	EPA SW846 Draft M0040/ Mod EPA 18	± 5	DI FS	± 30	ТМ	± 35	MAS/ PAS	100**
Aldehydes (1)	CARB 430/ CARB 430	± 15	DA FS	± 30	ТМ	± 30	MS/ PAS	100**
PAH (1)	CARB 429/ CARB 429	± 50	DA LCS	± 87	TM	± 50	LCS/ PAS	100**
Phenol	Mod EPA SW846 M0010/ EPA SW846 M8270	± 50	DA LCS	± 87	ТМ	± 50	LCS/ PAS	100**

^{*} Data used to calculate DQIs

DA - duplicate analysis

DI - duplicate injection

FS - field sample

LCS - laboratory control sample

MAS - method audit sample

MS - matrix spike

PAS - performance audit sample

TM - triplicate measurement at operating conditions A-1 and A-4

BURNER EXPERIMENTAL TRACK

Track Findings

- Gas-fired combustion is *much* cleaner than previously thought, so much so that the experiment needed to be redesigned to accommodate the lower emissions.
- There was no significant difference in air toxic emissions between using process gas and natural gas.
- The performance of the LDFB is comparable to that of the CDFB.

A detailed listing of the burner experimental track results is given in the appendix.

Location

This track was conducted at the BERL because it provides controlled, stable, and well-characterized operating conditions for full-scale burners. The BERL also features laser diagnostic and air emissions testing capabilities that allow complete characterization of industrial burner flames and emissions.

The burner itself is a 900 kW full-scale burner (see Figure 1). The BERL can be broken into two distinct sections: the furnace section and the convective section simulator (CSS). The walls of the furnace section are water-cooled and extract heat from the combustion gases via

^{**} Incomplete measurements will be repeated

^{1.} Target analytes listed in Table 4-1 of the QA Project Plan for ATM, June 28, 1995

radiation. From the furnace section, combustion gases flow to the quartz-lined CSS, which is designed to duplicate the average temperature drop seen in full-scale heaters.

Figure 1 - Burner Engineering Research Lab (BERL) Sample Ports Convective Cooling Section Mezzanine Level Hood Combustion Chamber Optics Table Burner Air Intake Manifold Fuel Inlet Ground Level Air Preheater Vertical Traverse

Much thought went into the design of the CSS. While the BERL is optimized for the study of flame structure, refinery process heaters are optimized for efficiency and economy. Because of this, a refinery process heater employs a convective section for additional heat extraction, a feature not needed in the BERL. Since previous kinetics studies indicated that a significant amount of reaction chemistry may occur in the convection section (this was verified in our study), a CSS was added to the BERL.

Although adding an actual convective section to the BERL would seem the most realistic option, this approach was subject to serious limitations. For the desired reactions to occur, the gas stream must remain within the convective section for an adequate length of time.

Constructing a convective section with sufficient gas residence time, yet scaled to the BERL, would have been very expensive. Also, since mixing rates in an actual convective section cannot be controlled, different areas of the flow stream cool at different rates. This would have made representative sampling impossible.

Instead of a convective section, we decided to construct a CSS. The CSS closely matched the temperature-time profiles of refinery process heaters over a range of mean cooling rates. Mixing was accomplished by adding a series of steps and miters to the walls of the CSS which created turbulence in the gas flow. Catalytic effects between the gas stream and the CSS were prevented by lining all parts of the CSS exposed to the gas stream with quartz. The CSS is shown in Figure 2.

Flow Control and Mestering Jacket Insulation

Test Section

Flow Control and Mestering Jacket Insulation

Flow Cultow Dikritorn

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Sample locations were chosen to ensure that the sample obtained represented the flue gas exhaust stream and desired sample conditions. Flue gas slipstreams were pulled from the BERL both before and after the CSS. This combined approach allowed the study of both flame and exhaust temperature/residence time on air toxics formation and destruction.

Analysis

Five sequences of tests were conducted at the BERL (See Table 2). Each of them was designed to map out a specific set of parameters and operating conditions. Table 2 gives an overview of the burner experimental track. A more complete description of each track, with a detailed breakdown of the burner experimental track results, is presented in the appendix.

Table 2 - BERL Sequence Descriptions

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Sequence A	CDFB1	Standard	Base case condition and minor deviations							
		Conditions								
Sequence B	CDFB	Failure Modes	High excess air, cold surface quenching, air							
_			maldistribution, and other conditions more							
			likely to result in poor combustion than the							
			conditions in Sequence A							
Sequence C	CDFB	Severe Failure	More severe conditions than Sequence B (e.g.,							
_		Modes	450% stoichiometric air, 75% stoichiometric air							
			throughout the combustion zone and convective							
			section simulator)							
Sequence D	LDFB ²	Severe Failure	Same severity as Sequence C							
Sequence E	CDFB	Extreme Failure	More severe conditions than sequence C							

(e.g. 50% stoichiometric air)

¹ Conventional Diffusion Flame Burner ² Low-NO_x Diffusion Flame Burner

Sequence A simulated baseline and variant conditions that might be expected in the typical operation of a process heater or boiler (see Figure 3). We hypothesized that by varying the fuel mixture and operating conditions, we would cause changes in the makeup of the emissions. We hoped that by studying these changes, we could then create a model that would predict how a gas-fired industrial process heater or boiler might behave under different operating conditions.

The results of Sequence A (and the subsequent few sequences) were surprising. The emission levels were uniformly low, regardless of the parameters we used. Variations in the results stemmed from random fluctuations--signal noise--around the detection limits, rather than from any adjustments we made. Most toxics were not detected, despite analytical techniques with detection limits ranging from 0.5-1 parts per billion (ppb) for most species, to about 0.1 parts per trillion (ppt) for 19 separate PAHs.

Single-ring aromatic emissions were generally low, within the 0.5-3 ppb range. Benzene was found in only 5 of the 13 Sequence A cases. Only one case, A12, with an increased heating value of 1500 Btu/scf, generated a concentration significantly higher than the detection limit. Since other runs with similar parameters did not produce a similar result (over five standard deviations away from the mean Sequence A levels), it is probable that A12 is a statistical outlier.

Formaldehyde and acetaldehyde measurements were higher, typically 5-50 ppb. However, aldehydes are notoriously difficult to quantify at these levels, and even a series of blanks registered between 20 and 70 ppb for both aldehyde species.

PAHs are of primary concern due to their carcinogenicity. Benzo(a)pyrene, often viewed as a "standard" PAH from a regulatory perspective, was not detected in any of the 13 Sequence A runs.

Naphthalene is difficult to measure, and tests for naphthalene are much less sensitive than those for other PAHs. In the BERL studies, the detection limit for naphthalene was 20 ppt, ~200 times greater than the other PAHs. Naphthalene was found in 1 of the thirteen runs, at 83 ppt. However, since naphthalene is not carcinogenic, its presence cannot be compared with its other, more carcinogenic cousins.

Since most toxic species were detected at levels near the detection limits and similar concentrations of these species were sometimes found in the blanks, many "hits" could be artifacts of the test, rather than actual detects. However, assuming that all hits did, in fact, detect the relevant species, in no cases were the estimated total refinery combustion emissions as high as 10 tons per year for any individual air toxic, nor as high as 25 tons per year for all toxics in aggregate (based on a total firing rate of 6000 MMBtu/hr, typical of petroleum refineries). See Figure 3A.

In no case did the total emissions for the 19 PAHs exceed 1 ton per year (Figure 3B), based on the 6000 MMBtu/hr typical-refinery firing rate.

Sequence A

Figure 3 - Sequence A: Standard Conditions

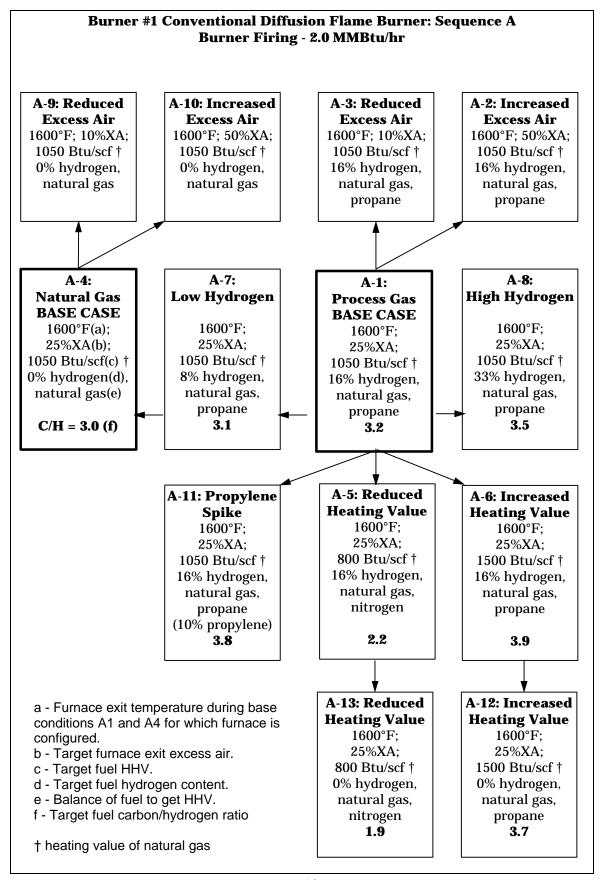
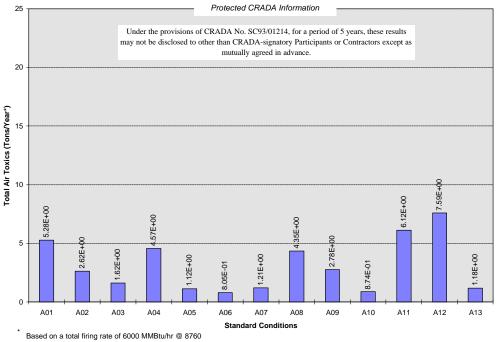


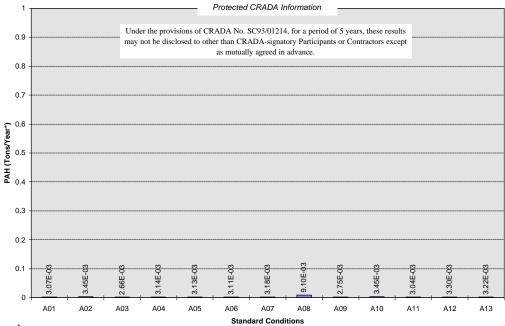
Figure 3A Conventional Diffusion Flame Burner - Sequence A Toxics Measurements



hours/year which is typical of a ca.250,000 bpd refinery

Note: ND value was used for all of the calculations.

Figure 3B Conventional Diffusion Flame Burner - Sequence A PAH Measurements



Based on a total firing rate of 6000 MMBtu/hr @ 8760 hours/year which is typical of a ca.250,000 bpd refinery

Sequence B

Given the very low levels of toxics produced in Sequence A, we redoubled our efforts to produce toxics in Sequence B, which simulated serious failures that might occur occasionally in a process heater or boiler. Figure 4 summarizes Sequence B.

Burner #1 Conventional Diffusion Flame Burner: Sequence B Burner Firing Rate - 2.0 MMBtu/hr **B-9: Cold Surface** B-8: Ethylene B-10: Severe Air A-11: Propylene Spike Quenching Maldistribution Spike 1600°F; 1600°F; 25%XA: 1600°F: 1600°F: 25%XA; 1050 BTU/scf† 1050 BTU/scf† 25%XA; 25%XA; 1050 BTU/scf† 16% hydrogen, 1050 BTU/scf† 16% hydrogen, natural natural gas, propane 16% hydrogen, natural gas, 16% hydrogen, gas, propane (8.4% propylene) propane natural gas, propane Block ½ air and fuel (18% ethylene) injectors A-1: Process Gas BASE CASE † heating value of 1600°F; 25%XA; 1050 BTU/scf† natural gas 16% hydrogen, natural gas, propane ** Introduce air leakage above combustion zone A-4: Natural Gas BASE CASE 1600°F; 25%XA; 1050 BTU/scf† 0% hydrogen, natural gas B-7a: Comb Zone SR<1* B-7a prop: Comb Zone SR<1* 1600°F; 25%XA(total**); 1600°F; 25%XA(total**); 1050 BTU/scf† 1100 BTU/scf† nat gas (8.4% propylene). *Comb Zone SR lowered nat gas *Comb Zone SR lowered to just before CO breakthrough to just before CO breakthrough B-7b: Comb Zone SR<<1* B-7b prop: Comb Zone SR<<1* 1600°F; 25%XA(total**); 1600°F; 25%XA(total**); 1050 BTU/scf† 1100 BTU/scf† nat gas *Comb Zone SR lowered past CO, nat gas (8.4% propylene). *Comb Zone SR lowered before HC, breakthrough past CO, before HC, breakthrough B-7a prop: Comb Zone SR<<<1* B-7c: Comb Zone SR<<<1* 1600°F; 25%XA(total**); 1600°F; 25%XA(total**); 1050 BTU/scf† 1100 BTU/scf† nat gas *Comb Zone SR lowered past HC nat gas (8.4% propylene). *Comb Zone SR lowered past HC breakthrough breakthrough

Figure 4 - Sequence B: Failure Modes

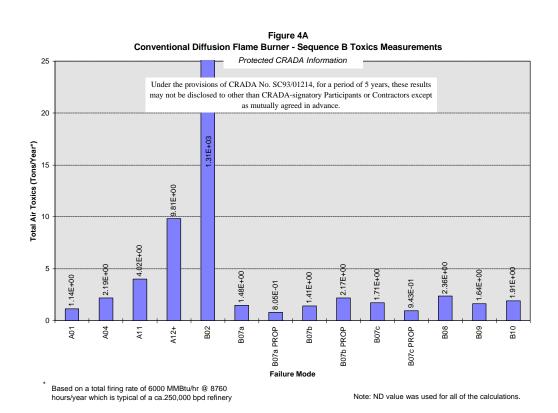
These Sequence B failure modes were expected to produce higher levels of air toxics than Sequence A. We were surprised to discover that this was not the case. In test after test, Sequence B modes failed to produce significantly greater levels of air toxics than found in Sequence A.

Once again, Benzo(a)pyrene was not detected. Benzene was typically 2 ppb or lower, with non-detects at limits as low as 0.2 ppb. The results were similar for all air toxic species studied.

Figures 4A and 4B show the air toxics and PAH emissions from the runs conducted in Sequence B, scaled up to the firing rate of a typical refinery.

The Sequence B results were cause for great concern. A disagreement of this magnitude between expected and actual result cast serious doubts on the validity of our study. (A closer examination of the field data and new kinetics models would later confirm our measurements, but at the time they had not been completed.) Questions were raised as to how effective a simulator the BERL was. Perhaps some sort of catalysis or other reaction within the BERL was destroying the toxic species.

We decided that the best course of action would be to reconfigure the burner analysis track. We had originally intended to test the BERL with a variety of different burner designs. However, all results would be rendered useless if there was a problem with the BERL itself. We decided to continue testing with the CDFB in the next sequence (Sequence C).



Protected CRADA Information Under the provisions of CRADA No. SC93/01214, for a period of 5 years, these results 0.9 may not be disclosed to other than CRADA-signatory Participants or Contractors except as mutually agreed in advance 0.8 0.7 0.3 0.2 3.95E A11 B10 404 B02 B07b B08 B09 401 412+ B07a PROP PROP B07c PROP Failure Mode Based on a total firing rate of 6000 MMBtu/hr @ 8760 hours/year which is typical of a ca.250,000 bpd refinery Note: ND value was used for all of the calculations.

Figure 4B Conventional Diffusion Flame Burner - Sequence B PAH Measurements

Sequence C

In Sequence C, we did not attempt to mimic real life situations. To validate our study, we had to demonstrate that the BERL was capable of producing air toxics. Because the main source of discrepancy between predicted and observed emissions concerned the levels of PAHs, we focused on detecting these species. Figure 5 lists the conditions of Sequence C.

To verify that the BERL itself was not destroying the PAHs, Sequence C also included measuring different levels of PAHs in nitrogen carrier gas as it passed through the CSS. Since levels at the inlet and outlet were roughly equivalent, it was clear that homogenous combustion, and not some physical feature of the CSS, was responsible for destroying the PAHs.

Sequence C repeated some Sequence B conditions, this time taking measurements at both the inlet and exit of the CSS. This provided valuable insight into the combustion chemistry. Figure 5B shows the PAH levels generated by the BERL in Sequence C. Run B2, with 350% stoichiometric air present throughout the BERL, generated PAHs that were found at very similar levels at both the CSS inlet and exit. Runs B12 and B13, with 75% stoichiometric air throughout the BERL, also showed roughly similar PAH levels before and after the CSS. (Note: The Sequence C runs focused on PAHs. As shown in Figure 5A, total air toxics were not measured.)

Run B7c, however, showed high levels of PAHs at the CSS inlet that were significantly reduced at its exit. In B7c, we introduced 50% stoichiometric air in the combustion zone and 125% in the CSS. This is strong evidence that post-flame reaction chemistry in the presence of oxygen can effectively destroy PAHs.

Sequence C also revealed that additional oxygen into the CSS, even when at temperatures significantly lower than seen in the furnace, reduced 4-ring and larger PAHs by 5 orders of magnitude, from 0.5 ppm to 0.005 ppb. When the air was held to a constant 75% throughout the BERL, no reduction of 4-ring and larger PAHs was seen. The chemical mechanism track later confirmed these findings and determined the mechanisms of the individual reactions.

Sequence D

Sequence D showed that emissions levels from Low-NOx Diffusion Flame Burners (LDFBs) were similar to those of Conventional Diffusion Flame Burners (CDFBs). The differences between the two were minimal, with both burners producing comparable amounts of air toxics under severe failure modes. Figure 6 summarizes Sequence D. Figures 6A and 6B show that, as with the Conventional Diffusion Flame Burner runs in Sequences A, B, and C, the LDFB runs of Sequence D produced low levels of air toxics and PAHs.

Sequence E

The final Sequence used the CDFB under conditions that would never be expected to occur under normal operations (Figure 7). Figures 7A and 7B show the resulting air toxics and PAH emission levels.

Under these conditions, such as 50% stoichiometric oxygen throughout the BERL, pollutant concentrations reached very high levels, matching those reported in some field observations. Run E2, with 60% stoichiometric air, produced especially high PAH levels. It is highly unlikely that there is anything special about the 60% ratio. Since Sequence E pushed the physical limits of the combustion process, this type of fluctuation is to be expected.

We welcomed these high results, for they again demonstrated that the BERL was capable of producing very high levels of toxics, and that the low toxics concentrations measured in previous sequences did not result from shortcomings in the experimental apparatus.

CHEMICAL MECHANISM TRACK

The chemical mechanism track established new chemical mechanisms by which air toxic species are produced and destroyed.

Track Findings

- New chemical kinetics models accurately predict the low emission results found at the BERL. There appear to be no lower limits to air toxics concentrations due to chemical kinetic constraints.
- These new models also support the BERL findings that the different compositions of natural and process gas appear to have minimal effect on flame structure and emissions.
- The main pathway to benzene in petroleum burners is through the interaction of two C3 species, rather than three C2 species as previously thought.
- New kinetic pathways to larger ring PAHs have been discovered. It was found that low levels of oxygen can promote PAH formation. In the past, it was thought that oxygen at any level inhibits PAH formation.

Figure 5: Sequence C: Severe Failure Modes

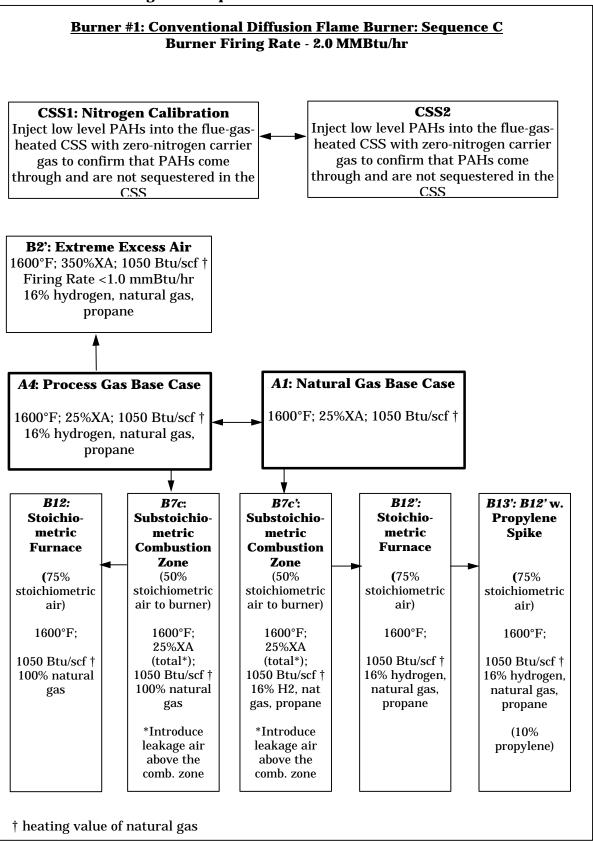
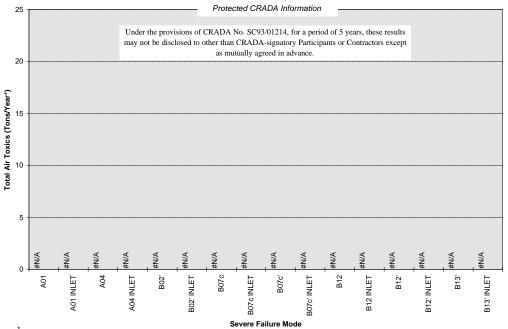


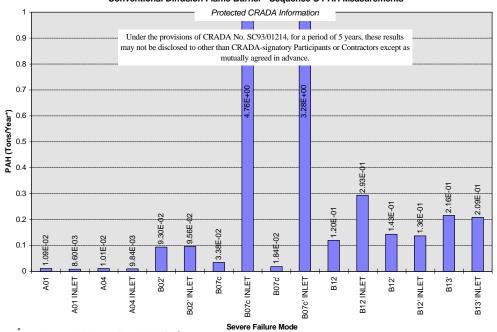
Figure 5A
Conventional Diffusion Flame Burner - Sequence C Toxics Measurements



Based on a total firing rate of 6000 MMBtu/hr @ 8760 hours/year which is typical of a ca.250,000 bpd refinery

Note: ND value was used for all of the calculations.

Figure 5B
Conventional Diffusion Flame Burner - Sequence C PAH Measurements

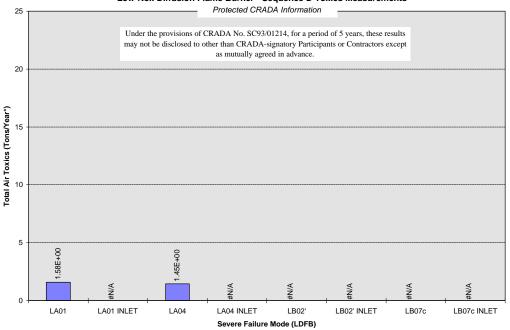


Based on a total firing rate of 6000 MMBtu/hr @ 8760 hours/year which is typical of a ca.250,000 bpd refinery

Burner #2 Low NOx Diffusion Flame Burner (LDFB): Sequence D Burner Firing Rate - 2.0 MMBtu/hr Lb2': Extreme Excess Air 1600°F; 350%XA; 1050 Btu/scf † Firing rate = 0.7 mmBtu/hr; 16% hydrogen, natural gas, propane LA4: Natural Gas Base Case LA1: Process Gas Base Case 1600°F; 25%XA; 1050 Btu/scf † 1600°F; 25%XA; 1050 Btu/scf † 16% hydrogen, natural gas, 100% natural gas propane LB7c: Substoichiometric **Combustion Zone** (50% stoichiometric air to burner) 1600°F; 25%XA (total*); 1050 Btu/scf † 100% natural gas * Introduce leakage air above † heating value of natural gas

Figure 6 - Sequence D: Severe Failure Modes (Low-NOx Flame Burner)

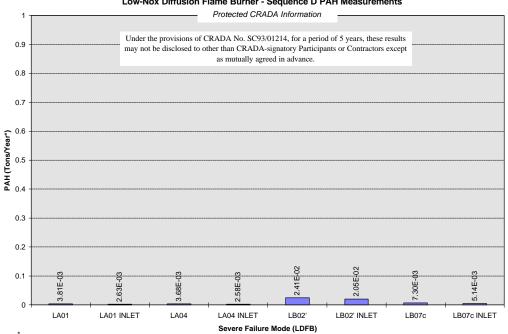
Figure 6A
Low-Nox Diffusion Flame Burner - Sequence D Toxics Measurements



Based on a total firing rate of 6000 MMBtu/hr @ 8760 hours/year which is typical of a ca.250,000 bpd refinery

Note: ND value was used for all of the calculations.

Figure 6B
Low-Nox Diffusion Flame Burner - Sequence D PAH Measurements



Based on a total firing rate of 6000 MMBtu/hr @ 8760 hours/year which is typical of a ca.250,000 bpd refinery

Figure 7 - Sequence E: Extreme Failure Modes

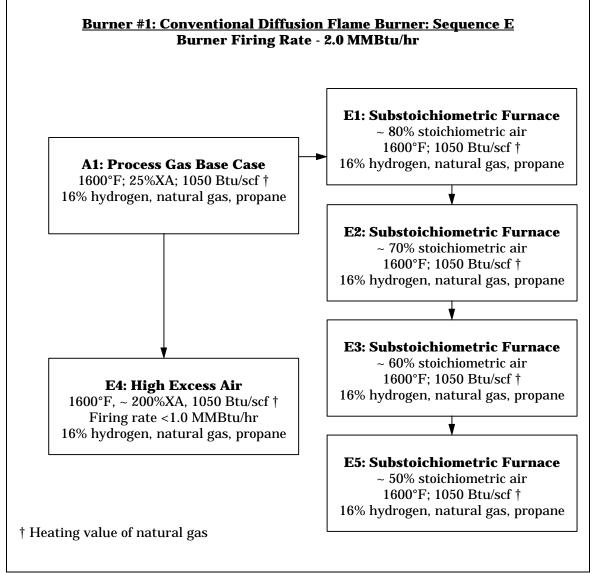
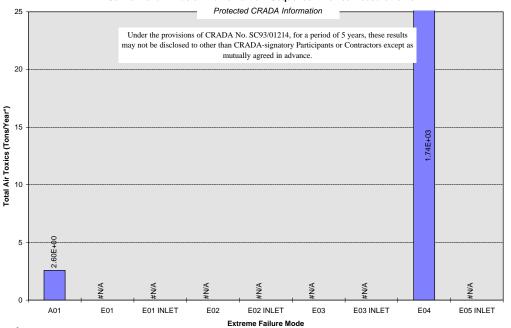


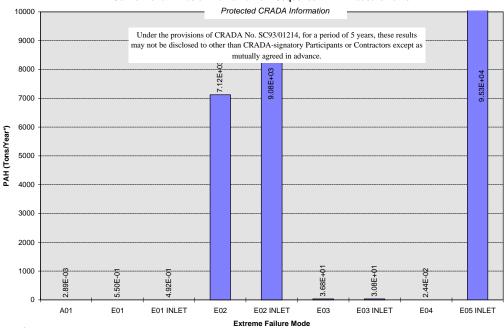
Figure 7A
Conventional Diffusion Flame Burner - Sequence E Toxics Measurements



* Based on a total firing rate of 6000 MMBtu/hr @ 8760 hours/year which is typical of a ca.250,000 bpd refinery

Note: ND value was used for all of the calculations.

Figure 7B
Conventional Diffusion Flame Burner - Sequence E PAH Measurements



Based on a total firing rate of 6000 MMBtu/hr @ 8760 hours/year which is typical of a ca.250,000 bpd refinery

Flame Structure Studies

Laboratory burner studies at both SNL and UCLA assisted the development of the chemical kinetics mechanisms. Although the laboratory burners were much smaller than either the BERL or commercial burners, they offered a degree of monitoring and control impossible to attain in larger facilities.

Studies at the Sandia Research Furnace assessed the effects of fuel composition and excess air on burner fluid mechanics and flame structure.

Studies at UCLA profiled selected toxic combustion byproducts, such as aromatics and PAHs in premixed and diffusion hydrocarbon flames. The premixed flame studies addressed regions of a process heater where mixing of fuel and air is rapid and occurs before combustion. Counterflow diffusion flames were used to simulate areas of a process heater where the limiting factor in combustion is the mixing of fuel and air.

Chemical Mechanism Development

Lawrence Livermore National Laboratory's main objective within Project 92-19 was to gain a better understanding of the chemical reactions that form and destroy air toxic species in process heaters and boilers. Data from the bench-scale experiments at UCLA were used to develop new chemical kinetic mechanisms. Together with the flame structure data produced at the BERL, these new mechanisms were used to develop models for predicting the formation and destruction of combustion byproducts.

The discovery of new kinetic mechanisms and the development of state-of-the art combustion models improves our understanding of how air toxics are formed and destroyed in industrial process heaters and boilers .

Aromatic Formation in Flames

Aromatic rings first evolve from the combination of resonantly stabilized free radicals. This occurs by three reaction pathways (See Figure 10). What is most significant in each of these pathways is the vital role that resonantly stabilized propargyl and 1-methylallenyl radicals play in the formation of aromatics. Prior to this work aromatic rings were thought to form primarily by the successive combination of three radicals containing two carbon atoms each. This study revealed the importance of the 3-carbon atom plus 3-carbon atom pathway.

PAH Formation in Flames

Once aromatics are formed, it becomes possible to form PAHs (Figure 11).

This study for the first time pieced together the important steps in this process of aromatics formation, including the key role played by oxygen in building polycyclic aromatics.

Validation of Kinetics Mechanisms

In premixed, laminar, burner-stabilized flames, the model reproduced the formation of single and multi-ring aromatics very well. The one exception was toluene, which the model over predicted by a factor of 6-10. This suggests that further work is needed in understanding and making the model reflect the benzyl consumption reactions.

In counterflow diffusion flames, one marked exception to the general agreement was that the measured concentration of the propargyl radical was a factor of ten higher than the model predictions. This led to a benzene concentration that was a factor of 40 higher than expected. Substituted benzenes such as toluene did not show an analogous increase. Changes in gas density, mechanism, and rate constants may account for the discrepancy between the measured and predicted benzene concentrations, and suggest further work must be done in this area (see Figures 12,13).

The validated chemical kinetics mechanisms were used to create models of the combustion processes found in small-scale and full-scale burner tests. Computations based on these models agree with the low emissions found in the BERL and suggest that there are no lower limits to the air toxics concentrations due to chemical kinetic constraints.

These models reinforce our findings that a commercial gas burner is a low toxics burner by its very design. Attempts to establish pathways where toxic species may be released suggest that the one way a toxic species might be released is where it escapes the furnace without mixing with air. This is consistent with the BERL Sequences C, D and E data showing significant levels of air toxics in fuel-rich conditions.

FIELD DATA ANALYSIS TRACK

The field data analysis track reviewed the data from previous field studies to relate the combined information from the previous two tracks with industrial real world experience. Cases where the field data did not agree with the study results were further examined to establish the cause of the disagreement. This track was performed by the PERF participants.

Findings

- There is a general agreement between field measurements and PERF results.
- The existing field data do not provide adequate information about operating conditions to make a detailed comparison between it and the PERF Study.
- Misleading emission factors in the field data resulted from differences in calculating the values of non-detects.
- Some deviations remain, especially in regard to PAHs and aldehydes. While we cannot disregard this data, it does not invalidate the general agreement between field and PERF results.

Comparing test data with field systems proved to be extremely complicated. The primary source of field data is the Western States Petroleum Association (WSPA) document "Pooled Source Testing of Combustion Devices: Database Users Guidance Manual" (January 1994), hereafter referred to as the WSPA database.

At first glance, the disagreement between the PERF and field data is striking. The WSPA database lists emission factors that are much higher than those either found at the BERL or predicted by the kinetics studies. A closer examination reveals that differences in the way non-detects are used accounts for much of the discrepancy between data sets.

Non-Detects

Every test has a detection limit. A result that is below this limit is given a result of "non-detect" (ND). An ND, however, does not indicate that the analyte was not present; it merely shows that the analyte was not detected.

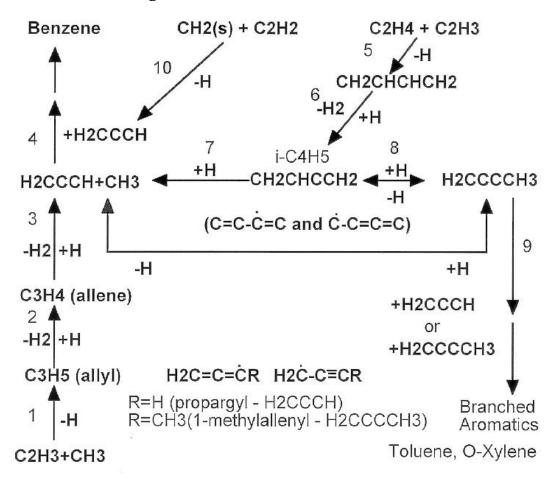


Figure 10 - Aromatic Formation in Flames

In the first pathway, a methyl radical combines with a vinyl radical to form an allyl radical (Path 1). The allyl radical then loses 2 hydrogen atoms to form a propargyl radical (Paths 2,3). Two propargyl radicals then combine to form benzene (Path 4).

In the second reaction pathway, a vinyl radical combines with an ethylene molecule to form a CH2CH2CHCH2 intermediate (Path 5). This intermediate loses a hydrogen atom to form 1,3-butadiene, and another H atom is removed to form the resonantly stabilized i-C4H5 species (Path 6). This either adds an H atom (Path 7), decomposing into a methyl and propargyl radical (which then self-combines as in pathway 1), or ejects another H atom to become a 1-methylallenyl radical (Path 8). This either combines with another 1-methylallenyl radical to become O-xylene or with a propargyl radical to form toluene (Path 9).

The final reaction pathway involves a singlet methylene insertion into acetylene (Path 10). This forms a propargyl radical which self-combines to form benzene.

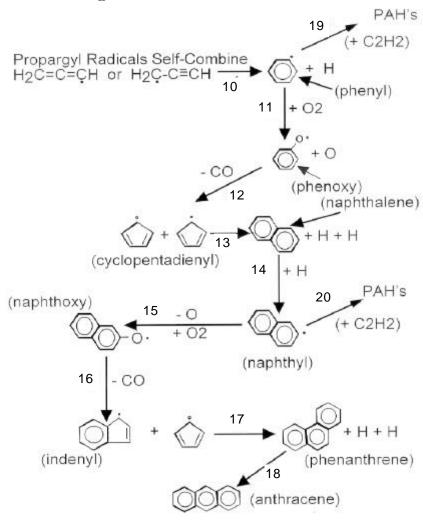


Figure 11 - PAH Formation in Flames

When combined with an oxygen molecule, the phenyl radical becomes a cyclopentadienyl radical and a CO-anion. Two cyclopentadienyl radicals then combine to form naphthalene (Paths 11-13). Once naphthalene is formed, it can lose a hydrogen atom to form a naphthyl radical (Path 14). Successive combinations with oxygen to form an indenyl radical (Paths 15,16). This radical then reacts with a cyclopentadiene radical to form phenanthrene, which isomerizes into anthracene (Paths 17,18).

An indenyl radical can also self-combine, or combine with other structures having cyclopentadienyl moiety to form still larger polycyclic aromatic hydrocarbons. The indenyl radical can also be formed by the reaction of acetylene with a benzyl radical (from toluene). Although this process is independent of oxygen, the other cyclopentadienyl radicals must still successfully compete with oxygen in order to form anthracene.

Figure 12 - Comparison of Stirred Reactor Results with Air Toxic Measurements

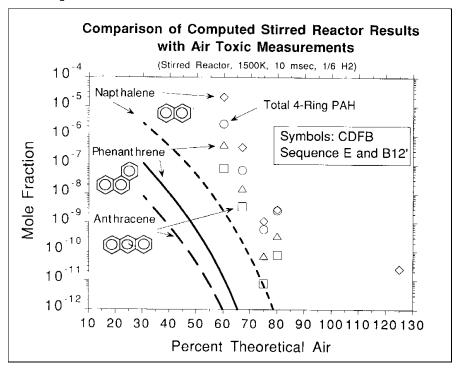
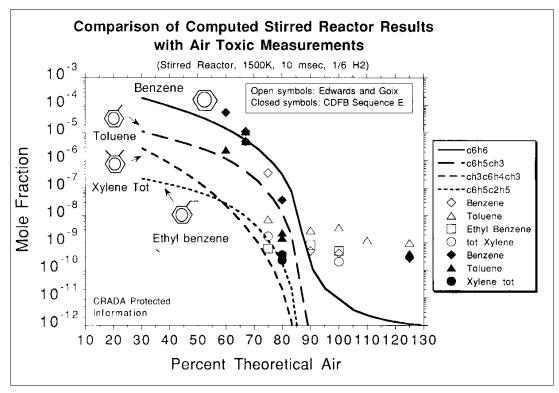


Figure 13 - Comparison of Computed Stirred Reactor Results with Air Toxic Measurements



Since NDs do not have numerical values, how they are included in statistical analyses is open to interpretation. In the WSPA studies, an ND was arbitrarily assigned a value of 1/2 the detection limit of the test. While this provides a conservative estimate for assessing risk, this method can give erroneously high emission factors.

For example, let's assume that three locations are tested for a given analyte. Two of the tests have detection limits of 2 (in this example, the numbers will be dimensionless.) The third test, however, follows a different method which has a detection limit of 20. In no case is the analyte detected. Using the 1/2 ND formula, the average emission factor is 4--twice the detection limit of the first 2 tests--even though the analyte has never been detected².

Evidence for this sort of bias is present in the WSPA database. Although the listed emission factors for benzene are between 1 x 10^{-5} to 5 x 10^{-5} lb/MMBtu, 11 of the 12 tests run with detection limits below these factors registered ND. Out of the 54 tests run, there were 52 results of "ND." The high percentage of ND results indicates that the WSPA emission factors are driven by non-detects and are almost certainly too high. The WSPA data for PAHs and formaldehyde display similar inconsistencies.

Comparing Field and BERL Data

Overall Comparisons

In order to compare WSPA and BERL data, the WSPA emission factors must be adjusted to compensate for the ND bias. Because WSPA data contain so few detects, the field results were augmented with separate industry results. Unfortunately, since this approach incorporates a significant degree of uncertainty, these emission factors should be treated as "best guesses."

The three pollutants listed in Table 3 were selected to represent three broad pollutant classes: benzene represents aromatics, formaldehyde represents products of incomplete combustion (PICs), and benzo(a)pyrene represents PAHs.

Table 3 - Typical emission factors based on the field and BERL data

	Typical Field Data Emission Factors	Typical BERL Emission Factors
	(lb/MMBtu)	(lb/MMBtu)
Formaldehyde	10-5 - 10-4	5x10 ⁻⁶ - 5x10 ⁻⁵
Benzene	10 ⁻⁶ - 10 ⁻⁵	$< 1x10^{-6} - 4x10^{-6}$
Benzo(a)pyrene	< 10-9 - 10-5	< 10-9

The data from the WSPA database precludes determining anything more than agreement on the same order of magnitude. Based on the available information, the field and BERL data are consistent for formaldehyde and benzene (or emissions of aromatics and PICs in general.)

The most apparent difference between the BERL and field data is the lack of high PAH emissions during the BERL tests under normal operating conditions. The BERL data overlap with the low end of the field data for benzo(a)pyrene, which corresponds to about 90% of the measurements reported in the WSPA database. The field data, however, show a variation in emissions of over four orders of magnitude, a range which is not duplicated in the BERL tests.

The only situations where the BERL produced PAHs as high as those measured in the highest field cases were in the failure modes in Sequences C, D, and E. These results suggest that extremely poor fuel-air mixing must have been present for the high field results. One possible

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² [(1/2)*(2)+(1/2)*(2)+(1/2)*(20)]/3=4

explanation might be the presence of liquid droplets in the fuel, but until more research is conducted, this remains speculation.

It is not known whether some of the field units being tested were operating under less than optimal conditions and, if so, how far from optimum were they being operated. However, since high levels of PAHs were found in some field burners, but not others, the data tends to support our findings that PAHs are not a necessary byproduct of burner operation.

CONCLUSION

The purpose of PERF 92-19 was to generate the best possible data using the best possible science for the best possible regulations. We believe that we have met this objective.

This study generated many surprises. The greatest surprise was the low emissions found at the BERL. So contrary to our expectations were these results that they initially cast doubt upon the validity of the entire study. The new chemical kinetics models ultimately verified the BERL findings and provided theoretical support for our assertion that a properly operating gas burner is a low toxics burner by its very design.

Both the conventional and low NOx burners tested at the BERL employ gas jets with high mixing potential, surrounded by an abundant supply of oxidant. The chemical kinetics mechanisms confirm that this type of burner will simply not produce high levels of toxic species.

PERF 92-19 also provides data that might be useful when diagnosing burners emitting abnormally high levels of air toxics. Since both the BERL data and the new chemical kinetics mechanisms indicate that high emissions result from either a compromised mixing potential or a limited supply of oxygen throughout the burner, an investigator may want to focus on factors that contribute to these conditions.

Initially, the field data appeared to disagree with the PERF results. However, upon closer examination, it was discovered that most of the discrepancy could be traced to different methods of data reduction, rather than to actual differences in emission levels. Although some discrepancies remain, the results of PERF 92-19 generally agree with existing field data.

A tremendous amount of thought and rigor that went into PERF 92-19. The overall agreement between each track in the study was a satisfying coda to four years of testing, modeling, and calculating. We believe this study for the first time lays a solid scientific foundation upon which regulations for industrial process heaters and boilers can be built.

Appendix A

Burner Experimental Track Process Data Summaries

TABLE A-1. CDFB SEQUENCE A PROCESS DATA SUMMARY

Test		Fuel C	ompos	ition (a)		LHV	HHV	Fuel Flo	w (d)	Н	eat Input	Primary	Air Flow	Primary	Overall		Tempe	erature
Condition	H2		C3H6		N2	(b)	(c)				(LHV)			Stoich.	Stoich.	Sampling		
				vol %	vol %		Btu/scf		scfm		MMBtu/hr	kg/s	scfm	Ratio	Ratio	Point	K	°F
A1-1	15.92	7.22	0.00	76.86	0.00	49.14		0.01198		589	2.010	0.2530	447	1.25	1.25	FE	1140	1593
A4.2	15.92	7.24	0.00	76.84	0.00	48.54		0.01189		F77	1.969	0.0407	444	1.25	1.25	CS FE	4440	1607
A1-2	15.92	7.24	0.00	70.84	0.00	48.54		0.01189		577	1.969	0.2497	441	1.25	1.25	CS	1148	1607
A1-3	15.88	7.25	0.00	76.87	0.00	49.08		0.01139		559	1.908	0.2403	425	1.25	1.25	FE	1146	1603
A1-3	13.00	1.23	0.00	10.01	0.00	49.00		0.01139		558	1.900	0.2403	423	1.25	1.23	CS	1140	1003
A1-4	15.84	7.23	0.00	76.93	0.00	49.16		0.01193		586	2.000	0.2521	445	1.25	1.25	FE	1147	1605
																CS		
A2	15.85	7.24	0.00	76.91	0.00	49.16		0.01182		581	1.983	0.2779	491	1.39	1.39	FE	1153	1616
																CS		
A3	15.97	7.27	0.00	76.76	0.00	49.15		0.01195		587	2.003	0.2218	392	1.10	1.10	FE	1168	1643
																CS		
A4-1	0.00	0.00	0.00	100.00	0.00	48.08		0.01220		588	2.007	0.2548	450	1.25	1.25	FE	1145	1602
110	0.00	0.00	0.00	400.00	0.00	40.00		0.04407			4.000	0.0504	440	4.05	4.05	CS	1110	4500
A4-2	0.00	0.00	0.00	100.00	0.00	48.08		0.01197		575	1.962	0.2501	442	1.25	1.25	FE CS	1143	1598
A4-3	0.00	0.00	0.00	100.00	0.00	48.01		0.01201		576	1.966	0.2508	443	1.25	1.25	FE	1136	1585
A4-3	0.00	0.00	0.00	100.00	0.00	40.01		0.01201		570	1.900	0.2300	443	1.25	1.23	CS	1130	1303
A4-4	0.00	0.00	0.00	100.00	0.00	48.11		0.01209		581	1.983	0.2526	446	1.25	1.25	FE	1143	1598
	0.00	0.00	0.00	100.00	0.00			0.0.200				0.2020		20	20	CS		.000
A4-5	0.00	0.00	0.00	100.00	0.00	48.37		0.01203		582	1.986	0.2535	448	1.25	1.25	FE	1143	1598
																CS		
(e)	12.11	0.00	0.00	78.22	9.67	41.13		0.01388		571	1.949	0.2464	435	1.25	1.25	FE	1133	1580
																CS		
A5-2	15.89	0.00	0.00	71.51	12.60	39.06		0.01496		585	1.997	0.2514	444	1.25	1.25	FE	1142	1596
40	45.00	04.00	0.00	40.75	0.00	47.95		0.04470		505	4.000	0.0440	407	4.05	4.05	CS	1175	4050
A6	15.92	34.33	0.00	49.75	0.00	47.95		0.01179		565	1.928	0.2419	427	1.25	1.25	FE CS	11/5	1656
A7	7.90	3.58	0.00	88.51	0.00	48.6		0.01198		582	1.986	0.2520	445	1.25	1.25	FE	1145	1602
\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	7.30	3.30	0.00	00.51	0.00	40.0		0.01130		302	1.300	0.2320	440	1.25	1.23	CS	1140	1002
A8	32.91	14.99	0.00	52.09	0.00	48.01		0.01208		580	1.980	0.2523	446	1.25	1.25	FE	1162	1632
																CS		
A9	0.00	0.00	0.00	100.00	0.00	48.08		0.01212		583	1.990	0.2225	393	1.10	1.10	FE	1156	1621
																CS		
A10	0.00	0.00	0.00	100.00	0.00	48.11		0.01205		580	1.980	0.2804	495	1.39	1.39	FE	1143	1598
						10.0-		2 2 4 4 5 =								CS		
A11-1	15.89	0.00	8.42	75.69	0.00	48.92		0.01185		580	1.980	0.2471	437	1.25	1.25	FE	1145	1602
A12	0.00	27.06	0.00	72.94	0.00	42.27		0.01240		586	2.000	0.2529	447	1.25	1.25	CS FE	1185	1674
AIZ	0.00	21.06	0.00	12.94	0.00	42.21		0.01240		000	2.000	0.2529	447	1.25	1.25	CS	1100	10/4
A13	0.00	0.00	0.00	76.21	23.80	31.81		0.01825		581	1.983	0.2531	447	1.25	1.25	FE	1129	1573
1 710	0.00	0.00	3.00	70.21	20.00	31.01		0.01020		301	1.500	5.2001	ודד	1.20	1.20	CS	1125	1070
a Fuel co			. (1															

a. Fuel composition from flow controller readings.b. Lower Heating Value

<sup>c. Higher Heating Value, values pending further information
d. Fuel flow rate calculated from air flow rate, fuel analysis, and excess air, scfm values pending further information</sup>

e. Intended to be test condition A5-1, but fuel flows not correct.

TABLE A-2. CDFB SEQUENCE B PROCESS DATA SUMMARY

Test		Fuel	Compositio	n (a)		LHV	HHV	Fuel Flow (d)		Hea	at Input	Primary Air Flow		Primary	Overall		Tempe	erature
Condition	H2	C3H8	Spike	N.G.	N2	(b)	(c)			(1	LHV)			Stoich.	Stoich.	Sampling		
	%	%	%	%	%	MJ/kg	Btu/scf	kg/s	scfm	KW	MMBtu/hr	kg/s	scfm	Ratio	Ratio	Point	K	°F
A1-5	16.00	7.10	0.00	76.90	0.00	49.15		0.01200		589	2.010	0.2524	445.9399209	1.25	1.25	FE	1140	1593
																CS		
A4-6	0.00	0.00	0.00	100.00	0.00	48.06		0.01230		589	2.010	0.2553	451	1.25	1.25	FE	1148	1607
																CS		
A4-7	0.00	0.00	0.00	100.00	0.00	48.06		0.01220		589	2.010	0.2552	451	1.25	1.25	FE	1146	1603
														-		CS		
A4-8	0.00	0.00	0.00	100.00	0.00	48.06		0.01220		584	1.993	0.2536	448	1.25	1.25	FE	1147	1605
												0.200				CS		
A11-2	16.00	0.00	C3H6/8.4	75.60	0.00	48 97		0.01190		582	1.986	0.2477	438	1.25	1.25	FE	1153	1616
/	10.00	0.00	0011070.1	70.00	0.00	10.01		0.01100		002	1.000	0.2111	100	1.20	1.20	CS	1100	1010
A12+	0.00	75.40	0.00	24 60	0.00	46.58		0.01020		474	1.618	0.2029	358	1.25	1.25	FE	1168	1643
/	0.00		0.00	2	0.00	10.00		0.0.020				0.2020	555	0	0	CS		10.0
B2	0.00	0.00	0.00	100.00	0.00	48.06		0.00370		179	0.611	0.2794	494	4.50	4.50	FE	1145	1602
52	0.00	0.00	0.00	100.00	0.00	40.00		0.00070		175	0.011	0.2754	404	4.00	4.00	CS	1170	1002
B7a	0.00	0.00	0.00	100.00	0.00	48.06		0.0122 ± 0.0003		586 ± 15	1.999 ± 0.05	0.1614(a)	285	0.79	1.25	FE	1143	1598
Ι Β/α	0.00	0.00	0.00	100.00	0.00	40.00		0.0122 ± 0.0003		300 ± 13	1.555 ± 0.05	0.1014(6)	200	0.73	1.20	CS	1170	1000
B7a prop	0.00	0.00	C3H6/8.4	01.60	0.00	47.65		0.0123 ± 0.0003		586 ± 15	1.999 ± 0.05	0.1304(a)	246	0.69	1.25	FE	1136	1585
Bra plop	0.00	0.00	03110/0.4	31.00	0.00	47.03		0.0123 ± 0.0003		300 ± 13	1.999 ± 0.05	0.1334(6)	240	0.03	1.23	CS	1130	1303
B7b	0.00	0.00	0.00	100.00	0.00	19.06		0.0122 ± 0.0003		506 ± 15	1.999 ± 0.05	0.1212(0)	214	0.60	1.25	FE	1143	1598
6/6	0.00	0.00	0.00	100.00	0.00	40.00		0.0122 ± 0.0003		300 ± 13	1.999 ± 0.05	0.1213(6)	214	0.00	1.25	CS	1143	1596
B7b prop	0.00	0.00	C3H6/8.4	01.60	0.00	47.65		0.0123 ± 0.0003		506 ± 15	1.999 ± 0.05	0.1104(a)	195	0.55	1.25	FE	1143	1598
B/D blob	0.00	0.00	C3F10/6.4	91.00	0.00	47.03		0.0123 ± 0.0003		300 ± 13	1.999 ± 0.05	0.1104(6)	195	0.55	1.25	CS	1143	1596
B7c-1	0.00	0.00	0.00	100.00	0.00	49.06		0.0122 ± 0.0003		E0C . 1E	1.999 ± 0.05	0.0070(a)	173	0.48	1.25	FE	1133	1580
B/C-1	0.00	0.00	0.00	100.00	0.00	40.00		0.0122 ± 0.0003		300 ± 13	1.999 ± 0.05	0.0979(6)	173	0.46	1.25	CS	1133	1360
DZa nran	0.00	0.00	C3H6/8.4	91.60	0.00	47.CE		0.0400 . 0.0000		FOC . 4F	1.999 ± 0.05	0.0004(a)	457	0.44	1.25	FE	1142	1596
B7c prop	0.00	0.00	C3H6/8.4	91.60	0.00	47.00		0.0123 ± 0.0003		000 ± 10	1.999 ± 0.05	0.0891(e)	157	0.44	1.25		1142	1596
- B0	40.00	0.00	00114/47.0	00.40	0.00	40.0		0.04400		504	4.000	0.0400	101	4.05	4.05	CS	4475	4050
B8	16.00	0.00	C2H4/17.9	66.10	0.00	49.2		0.01180		581	1.983	0.2439	431	1.25	1.25	FE	1175	1656
B0	40.00	7.46	0.00	70.00	0.00	10.15		0.04400		500	4.000	0.0400	110	4.05	4.05	CS	4445	4000
B9	16.00	7.10	0.00	76.90	0.00	49.15		0.01180		580	1.980	0.2492	440	1.25	1.25	FE	1145	1602
—																CS		
B10	16.00	7.10	0.00	76.90	0.00	49.15		0.00740		363	1.239	0.1559	275	1.25	1.25	FE	1162	1632
			n flow contro													CS		

a. Fuel composition from flow controller readings.

b. Lower Heating Value

<sup>c. Higher Heating Value, values pending further information
d. Fuel flow rate calculated from air flow rate, fuel analysis, and excess air, scfm values pending further information</sup>

e. Primary Air

TABLE A-3. CDFB SEQUENCE C PROCESS DATA SUMMARY

Test	F	uel Comp	osition	(a)	LHV	HHV	Fuel Flo	ow (e)	He	eat Input	Primary	Air Flow	Primary	Overall		Tempe	erature		
Condition	H2	C3H8(a)	C3H6	N.G.(b)	(c)	(d)				(LHV)						Stoich.	Sampling		
	vol %	vol %	vol %	vol %	MJ/scf	Btu/scf	kg/s	scfm	KW	MMBtu/hr	kg/s	scfm	Ratio	Ratio	Point	K	°F		
A1-6	16.0	7.2	0.0	76.9	49.4	1100	0.0117	36.5	577	1.969	0.248	438	1.25	1.25	FE	1144	1600		
															CS	660	728		
A4-9	0.0	0.0	0.0	100.0	48.3	1105	0.0121	36.7	583	1.989	0.253	447	1.25	1.25	FE	1139	1591		
															CS	652	714		
B2'	15.9	7.2	0.0	76.9	49.4	1103	0.0041	12.7	203	0.693	0.313	553	4.50	4.50	FE	773	932		
															CS	660	728		
B7c-2	0.0	0.0	0.0	100.0	48.3	1105	0.0117	35.5	565	1.928	0.098	173	0.50	1.25	FE	1125	1566		
															CS	654	718		
B7c'	20.1	3.5	0.0	76.5	50.1	1010	0.0102	35.2	513	1.750	0.088	155	0.50	1.25	FE	1108	1535		
															CS	652	714		
B12	0.0	0.0	0.0	100.0	48.3	1105	0.0115	34.9	555	1.894	0.144	254	0.75	0.75	FE	968	1283		
															CS	623	662		
B12'	16.0	7.1	0.0	76.9	49.4	1100	0.0112	34.9	554	1.890	0.142	251	0.75	0.75	FE	969	1285		
															CS	655	719		
B13'	16.5	0.0	5.1	78.4	49.5	1016	0.0114	38.7	565	1.928	0.145	256	0.75	0.75	FE	971	1288		
															CS	656	721		

a. Not including propane in the natural gas.

b. Natural gas composition on separate table.

c. Lower Heating Value.

d. Higher Heating Value.

e. Fuel flow calculated from air flow, air moisture content, stoichiometric ratio, and fuel composition.

f. In cases having secondary air, it was introduced by adjusting the furnace pressure to less than atmospheric, allowing air to enter through four 51 mm wide x 267 mm high slots located on the North, South, East and West sides of the furnac, with their centers at a height of 1.44 m above the burner.

TABLE A-4. CDFB SEQUENCE E PROCESS SUMMARY

Test	Fuel	Composi	ition (a)	LHV	HHV	Fuel Flov	Fuel Flow (e)		Heat Input		Air Flow	Primary	Overall		Tempe	erature
Condition	H2	C3H(a)	N.G.(b)	(c)	(d)				₋HV)			Stoich.	Stoich.	Sampling		
	vol %	vol %	vol %	MJ/scf	Btu/scf	kg/s	scfm	KW	MMBtu/hr	kg/s	scfm	Ratio	Ratio	Point	K	°F
A1-7	16.0	7.1	76.9	49.2	1096	0.01170	36.5	574	1.96	0.248	438	1.25	1.25	FE	1053	1435
														CS	654	718
E4	16.0	7.1	76.9	49.2	1096	0.00420	13.1	206	0.70	0.213	376	3.0	3.0	FE	818	1012
														CS	675	755
E1	16.0	7.1	76.9	49.2	1096	0.0119 ± 0.0003	37.1 ± 0.94	586 ± 15	2.00 ± 0.05	0.161	284	0.80 ± 0.025	0.80 ± 0.025	FE	948	1247
														CS	693	788
E2	16.0	7.1	76.9	49.2	1096	0.0119 ± 0.0003	37.1 ± 0.94	586 ± 15	2.00 ± 0.05	0.122	216	0.60 ± 0.025	0.60 ± 0.025	FE	855	1080
														CS	676	757
E3	16.0	7.1	76.9	49.2	1096	0.0119 ± 0.0003	37.1 ± 0.94	586 ± 15	2.00 ± 0.05	0.134	237	0.67 ± 0.025	0.67 ± 0.025	FE	888	1139
														CS	689	781
E5	16.0	7.1	76.9	49.2	1096	0.0119 ± 0.0003	37.1 ± 0.94	586 ± 15	2.00 ± 0.05	0.088	155	0.44 ± 0.025	0.44 ± 0.025	FE	816	1009
															·	

a. Not including propane in the natural gas.

b. Natural gas composition on separate table.

c. Lower Heating Value

d. Higher Heating Value, values pending further information

e. Fuel flow for cases A1 and E4 calculated from the air flow, air moisture content, stoichiometric ratio (excess oxygen), and fuel composition. When running the substoichiometric cases, E1, E2, E3, and E5, the fuel flowrate was first adjusted to give the correct excess oxygen (4.6 vol %, dry) at the air flowrate corresponding to 2 million Btu/hour (586 kW) and 25% excess air, then the air flowrate was reduced to give the desired stoichiometric ratio.

TABLE A-5. LDFB SEQUENCE D PROCESS DATA SUMMARY

Test	Fu	iel Compos	sition	LHV	HHV	Fuel Flo	ow (e)	Н	Heat Input Primary Air Flow		Primary	Overall		Temperature		
Condition	H2	C3H8 (a)	N.G. (b)	(c)	(d)				(LHV)				Stoich.	Sampling		
	%	%	%	MJ/kg	Btu/scf	kg/s	scfm	KW	MMBtu/hr	kg/s	scfm	Ratio	Ratio (f)	Point	K	°F
LA1	15.90	7.10	77.00	49.4	1097	0.0119	37.2	585	1.996	0.251	444	1.25	1.25	FEe	1072	1470
														CS	680	765
LA4	0.00	0.00	100.00	48.3	1099	0.0121	36.9	585	1.996	0.254	449	1.25	1.25	FEe	1097	1515
														CS	655	720
LB2'	16.00	7.00	77.00	49.4	1094	0.0041	12.9	204	0.696	0.209	369	3.0	3.0	FEe	762	912
														CS	605	630
LB7c	0.00	0.00	100.00	48.3	1099	0.0122	37.3	588	2.006	0.102	180	0.50	1.25e	FEe	1070	1467
														CS	644	699

a. Not including propane in the natural gas.

b. Natural gas composition on separate table.

c. Lower Heating Value.

d. Higher Heating Value.

e. Fuel flow calculated from air flow, air moisture content, stoichiometric ratio, and fuel composition.

f. Secondary air was introduced by adjusting the furnace pressure to less than atmospheric, allowing air to enter through four

⁵¹ mm wide x 267 mm high slots located on the North, South, East and West sides of the furnac, with their centers at

a height of 1.44 m above the burner.

Table A6. Summary of Air Toxics Emissions Tests

			N	No. of Analysi	s		
Test Condition	Run.	Sequence	PAH	Aldehydes	Heavy VOCs	Fuel Type	Description
A01	1	SEQ A	1	3	3	Process Gas	Base Case
A01	2	SEQ A	1	0	3	Process Gas	Base Case
A01	3	SEQ A	1	3	3	Process Gas	Base Case
A01	4	SEQ A	0	3	3	Process Gas	Base Case
A02	1	SEQ A	1	1	1	Process Gas	Increased Excess Air
A03	1	SEQ A	1	1	1	Process Gas	Reduced Excess Air
A04	1	SEQ A	1	2	3	Natural Gas	Base Case
A04	2	SEQ A	1	3	3	Natural Gas	Base Case
A04	3	SEQ A	1	3	3	Natural Gas	Base Case
A04	4	SEQ A	0	0	3	Natural Gas	Base Case
A04	5	SEQ A	0	4	0	Natural Gas	Base Case
A05	1	SEQ A	1	1	1	Process Gas	Reduced Heating Value
A05	2	SEQ A	1	1	1	Process Gas	Reduced Heating Value
A06	1	SEQ A	1	1	1	Process Gas	Increased Heating Value
A07	1	SEQ A	1	1	1	Process Gas	Low Hydrogen
A08	1	SEQ A	1	1	1	Process Gas	High Hydrogen
A09	1	SEQ A	1	1	1	Natural Gas	Reduced Excess Air
A10	1	SEQ A	1	1	1	Natural Gas	Increased Excess Air
A11	1	SEQ A	1	1	1	Process Gas	Propylene Spike
A12	1	SEQ A	1	2	1	Natural Gas	Increased Heating Value
A13	1	SEQ A	1	1	1	Natural Gas	Reduced Heating Value
A01	5	SEQ B	1	4	2	Process Gas	Base Case
A04	6	SEQ B	1	3	3	Natural Gas	Base Case
A04	7	SEQ B	1	2	2	Natural Gas	Base Case
A04	8	SEQ B	1	2	2	Natural Gas	Base Case
A11	2	SEQ B	1	2	2	Process Gas	Propylene Spike
A12+	1	SEQ B	1	2	2	Natural Gas	Increased Heating Value
B02	1	SEQ B	1	2	2	Natural Gas	Extreme Excess Air - Firing Rate < 1.0 MMBtu/hr
B07a	1	SEQ B	1	2	2	Natural Gas	Combustion Zone Stoichiometric Ratio <1 - just before CO breakthrough
B07a PROP	1	SEQ B	1	2	2	Natural Gas	Combustion Zone Stoichiometric Ratio <1 with propylene spike - just before CO breakthrough
B07b	1	SEQ B	1	2	2	Natural Gas	Combustion Zone Stoichiometric Ratio <1 - past CO, before HC breakthrough
B07b PROP	1	SEQ B	1	2	2	Natural Gas	Combustion Zone Stoichiometric Ratio <1 with propylene spike -past CO, before HC breakthrough
B07c	1	SEQ B	1	2	2	Natural Gas	Combustion Zone Stoichiometric Ratio <1 - past HC breakthrough
B07c PROP	1	SEQ B	1	2	2	Natural Gas	Combustion Zone Stoichiometric Ratio <1 with propylene spike - past HC breakthrough
B08	1	SEQ B	1	2	2	Process Gas	Ethylene Spike
B09	1	SEQ B	1	2	2	Process Gas	Cold Surface Quenching
B10	1	SEQ B	1	2	2	Process Gas	Severe Air Maldistribution - block 1/2 air and
A01 INLET	6	SEQ C	1	0	0	Process Gas	fuel injectors Base Case
A04	9	SEQ C	1	0	0	Natural Gas	Base Case
A04 INLET	9	SEQ C	1	0	0	Natural Gas	Base Case
A01	6	SEQ C	1	0	0	Process Gas	Base Case

			N	lo. of Analysi	is		
Test Condition	Run.	Sequence	PAH	Aldehydes	Heavy VOCs	Fuel Type	Description
B02'	1	SEQ C	1	0	0	Process Gas	Extreme Excess Air - Firing Rate < 1.0 MMBtu/hr
B02' INLET	1	SEQ C	1	0	0	Process Gas	Extreme Excess Air - Firing Rate < 1.0 MMBtu/hr
B07c	2	SEQ C	1	0	0	Natural Gas	Comb Zone SR<1 - past HC breakthrough
B07c'	1	SEQ C	1	0	0	Process Gas	Combustion Zone Stoichiometric Ratio <1 - past HC breakthrough
B07c INLET	2	SEQ C	1	0	0	Natural Gas	Combustion Zone Stoichiometric Ratio <1 - past HC breakthrough
B07c' INLET	1	SEQ C	1	0	0	Process Gas	Combustion Zone Stoichiometric Ratio <1 - past HC breakthrough
B12	1	SEQ C	1	0	0	Natural Gas	Combustion Zone Stoichiometric Ratio <.75 - total furnace
B12'	1	SEQ C	1	0	0	Process Gas	Combustion Zone Stoichiometric Ratio <.75 - total furnace
B12 INLET	1	SEQ C	1	0	0	Natural Gas	Combustion Zone Stoichiometric Ratio <.75 - total furnace
B12' INLET	1	SEQ C	1	0	0	Process Gas	Combustion Zone Stoichiometric Ratio <.75 - total furnace
B13'	1	SEQ C	1	0	0	Process Gas	Combustion Zone Stoichiometric Ratio <.75 - total furnace with propylene spike
B13' INLET	1	SEQ C	1	0	0	Process Gas	Combustion Zone Stoichiometric Ratio SR<.75 - total furnace with propylene spike
LA01	1	SEQ D	1	3	3	Process Gas	Base Case
LA01 INLET	1	SEQ D	1	0	0	Process Gas	Base Case
LA04	1	SEQ D	1	3	3	Natural Gas	Base Case
LA04 INLET	1	SEQ D	1	0	0	Natural Gas	Base Case
LB02'	1	SEQ D	1	0	0	Process Gas	Extreme Excess Air - Firing Rate < 1.0 MMBtu/hr
LB02' INLET	1	SEQ D	1	0	0	Process Gas	Extreme Excess Air - Firing Rate < 1.0 MMBtu/hr
LB07c	1	SEQ D	1	0	0	Natural Gas	Combustion Zone Stoichiometric Ratio ~ 0.50
LB07c INLET	1	SEQ D	1	0	0	Natural Gas	Combustion Zone Stoichiometric Ratio ~ 0.50
A01	7	SEQ E	1	3	3	Process Gas	Base Case
E01	1	SEQ E	1	0	2	Process Gas	Combustion Zone Stoichiometric Ratio ~ 0.80 - total furnace
E01 INLET	1	SEQ E	1	0	0	Process Gas	Combustion Zone Stoichiometric Ratio ~ 0.80 - total furnace
E02	1	SEQ E	1	0	2	Process Gas	Combustion Zone Stoichiometric Ratio ~ 0.70 - total furnace
E02 INLET	1	SEQ E	1	0	0	Process Gas	Combustion Zone Stoichiometric Ratio ~ 0.70 - total furnace
E03	1	SEQ E	1	0	2	Process Gas	Combustion Zone Stoichiometric Ratio ~ 0.60 - total furnace
E03 INLET	1	SEQ E	1	0	0	Process Gas	Combustion Zone Stoichiometric Ratio ~ 0.60 - total furnace
E04	1	SEQ E	1	2	2	Process Gas	Extreme Excess Air - Firing Rate < 1.0 MMBtu/hr
E05 INLET	1	SEQ E	1	0	0	Process Gas	Combustion Zone Stoichiometric Ratio ~ 0.50